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International Research Project on the Effects of Chemical
Ageing of Polymers on Performance Properties

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**CORRELATION OF CHEMICAL AND
PHYSICAL TEST DATA FOR THE
ENVIRONMENTAL AGEING
OF COFLON (PVDF)**

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CONTENTS

SYNOPSIS

- 1 INTRODUCTION**
- 2 COMMENT**
- 3 COLLATED RESULTS AND DISCUSSION**
 - 3.1 Fluid F (wet H₂S mixture + amine)**
 - 3.1.1 Mechanisms**
 - 3.1.2 Conclusions for Fluid F**
 - 3.2 Fluid A (methanol)**
 - 3.2.1 Mechanisms**
 - 3.2.2 Conclusions for Fluid A**
 - 3.3 Fluid G (methanol + amine)**
 - 3.3.1 Mechanisms**
 - 3.3.2 Conclusions for Fluid G**
- 4 FURTHER DISCUSSION**
- 5 GENERAL CONCLUSIONS**

ACKNOWLEDGEMENTS

REFERENCES

APPENDIX 1

SYNOPSIS

A large number of different tests have now been performed on Coflon by MERL and TRI. All data obtained have been reviewed with the objectives of identifying trends caused by various exposures and possible correlations between different mechanical, physical and analytical tests. The intent was to provide a means of establishing methodology and most useful test procedures that will best characterise flexible pipe service life. As this should be based on an understanding of underlying chemical and morphological mechanisms at work, some effort has been made to justify these in the light of analytical data obtained.

This review has concentrated on data from the chemically-hostile Fluid F, Fluid A and Fluid G exposures, against a backcloth of deplasticisation known to be brought about by other fluids.

Caveats are made concerning the validity of making comparisons between some tests. Allowing for these, a possible correlation has been identified for Fluid F exposures, between fatigue crack growth resistance, crystallinity level and fluorine content. Lack of data prevented this correlation being investigated for the other fluids. Crack growth resistance apparently quantifies chemical changes which occur in Coflon. It has also been found that very low tensile strain levels can indicate when failure is of a brittle mode. Modulus changes can be informative for indicating deplasticisation, fluid absorption (replasticisation) and crystallisation changes - all physico-chemical effects: they can also indicate the presence of low molecular weight species following chain scission due to ageing.

In summary, the data obtained suggest that fatigue crack growth assessments at somewhat accelerated conditions provide a basic materials test which can follow chemical changes, but tensile strain values can be more sensitive to chemical ageing-induced brittle failure, and comparison of fatigue and modulus data can indicate whether changes are for physico-chemical or chemical reasons.

1 INTRODUCTION

This report aims to identify correlations between mechanical property changes and chemical/morphological structure changes for Coflon. It is intended both to illustrate the overall methodology and to indicate the testing that needs to be undertaken in order to obtain correlations. Many fluid exposures have now been carried out on Coflon during the project and many data generated as a result. The report summarises the changes observed in mechanical and physical properties and relates these as well as possible to the chemistry thought to be occurring during ageing. For this purpose, data have been collated from already-issued MERL and TRI technical and progress reports.

Most of the mechanical testing of aged testpieces has been performed soon after the completion of the exposure; however, there is of necessity a delay in obtaining chemical analysis of the same testpieces, so that more physical than chemical data are shown.

Three fluids have so far caused measurable deterioration of Coflon, these being: methanol (Fluid A), a methanol and amine mixture (Fluid G), and a mixture of methane, carbon dioxide gas and hydrogen sulphide gas plus aqueous amine (Fluid F). Only the effects of these fluids will be dealt with in any detail in this report, although other fluids are assessed to give relevant background information.

Relevant test data collated here include: tensile modulus and related properties, mode of sample failure at break, fracture toughness, fatigue crack growth rate and resistance, stress relaxation rate, permeation coefficients, % crystallinity and molecular weight distributions together with changes in fluorine levels, and other observations where appropriate. However, not all of these were obtained for every ageing condition. Because of the wide range of tests employed, and the different ways in which their results are obtained, the following section has been included to serve as a background for making comparisons.

2 COMMENT

For Coflon, the concept of correlating changes in PVDF chemistry and morphology with property changes and, ultimately, flexible pipe performance forms the crux of the project. This report points out from observations made the limited areas where similar trends are seen in more than one parameter. Writing it has also indicated to the reviewers some of the factors which must be addressed in making comparisons. For example, with aged specimens:

- crack growth fatigue measurements can be influenced by the sharpness of the crack tip, which undoubtedly lessens as the test progresses. With aged specimens, the timing of making the cut (before or after ageing) is also a factor: if made after ageing, it may cut through any aged 'skin' at the crack tip.

- a mechanical property result applying across the whole specimen will be less sensitive to local changes than an X-ray diffraction crystallinity level applying to a finite depth in the sample surface (to a maximum extent of 1.5-2mm).
- elemental analysis and EDAX data provide a profile of e.g. fluorine content across a specimen section, which for an aged sample could indicate that a conjugated or crosslinked skin had formed, whereas GPC is also providing an elegant measurement of crosslinking gives data which are averaged over the whole specimen.

Returning to correlation aspects, the next section indicates comparisons possible to date, taking into account some of the caveats above. In particular the methanol exposures showed how the application of strain accelerated deterioration by causing transverse cracks which in turn allowed methanol absorption to be completed more quickly: however, even in the absence of strain, complete disintegration eventually occurred for other specimens. However, it is not known whether, in situations where deterioration is less catastrophic, effects of stresses and strain (or residual stresses/strains as, with time, some of these dissipate to form permanent set) increase the extent of deterioration as well as the rate. It may be that strain effects are most important during early stages of ageing (or service) as, from stress relaxation measurements obtained in the project, it can be estimated that 75% of the original applied force will be lost in a matter of weeks.

3 COLLATED RESULTS AND DISCUSSION

By comparing benign gas mixtures such as Fluid B with deplasticisation experiments, (e.g. 2 weeks at 100C at atmospheric pressure in nitrogen) it was concluded that these gases at high pressures (HP) cause (a) deplasticisation and, (b) at the same time, some replasticisation from the gas at liquid-like densities. It is assumed that this phenomenon is a backcloth for all of the other HP gaseous fluid exposures. Hence each table of results includes unaged and deplasticised values as control data.

The compositions of the fluids used for ageing were selected from the standard references, viz.:

<u>Fluid</u>	<u>Component mixture</u>
A	Methanol (CH ₃ OH)
B	97/3 CH ₄ /CO ₂ with H ₂ O (v)
C	97/3 CH ₄ /CO ₂ dry
D	94/5/1 CH ₄ /CO ₂ /H ₂ S dry
E	94/5/1 CH ₄ /CO ₂ /H ₂ S with H ₂ O (v)
F	As fluid E plus 1% ethylene diamine
G	As fluid A plus 1% ethylene diamine
H	As fluid B plus 1% ethylene diamine
I	35/35/20/10 Heptane/cyclohexane/toluene/ 1-propanol
J	Water + 1% ethylene diamine

3.1 Fluid F (wet H₂S mixture + amine)

The full chemical composition of Fluid F is: 94/5/1 CH₄/CO₂/H₂S with saturated water vapour, the water containing 1% of ethylene diamine. Exposures were carried out at 5000 psi with the testpieces in the vapour phase, not the liquid.

Table 1 summarises the property and analytical results for Fluid F exposures at a variety of temperatures and durations. Some variation was noted in unaged results from different batches, so superscripts are used to indicate which control value should be employed for comparison purposes for each ageing test.

It will be seen that Fluid F ageing of samples from Coflon Batch 2 was much more hostile than for samples from any of the other three batches.

100C exposures

Deplasticisation had caused almost a doubling of modulus and a decrease in crack growth rate. Fluid F ageing at 100°C initially caused a decrease in modulus after 1 month followed by a slight increase after 3 months and a further increase after 6 months, with the modulus now back to its original value. Figure 1 shows the overall effects of Fluid F ageing at the various times and temperatures employed for earlier tests on fatigue crack growth rate; crack growth rate was significantly increased after 3 months exposure at 100C compared to the control rate (of either completely unaged or, especially, deplasticised material) - specific comparisons in Table 1 have been made between rates at a common J value (2kJ/m²) (usually requiring extrapolations to be made). The crack growth resistance (values for J when the growth rate is 10nm/c (c=cycle), an empirically chosen rate always on the steep section of the plot - see Figure 1) is perhaps more informative, increasing with deplasticisation and decreasing with the Fluid F exposure for the plots shown. However, after 6 months at 100C (not shown in Figure 1), the crack growth resistance was now greater than the unaged value (Table 1).

Some discoloration in the form of patchiness rather than overall darkening has occurred, but only after the 3 and 6 month exposures.

120C exposures

After ageing at 120C, modulus showed a general tendency to increase although not in a uniform or continuous manner. Partly brittle failure occurred with the Batch 2 sample tested after 4 weeks exposure. (NB. Only this batch of material showed this change and those below.) This was evidenced for this sample as a significant decrease in ultimate tensile strain or, more particularly, by the small difference between yield strain and ultimate strain. This mode of failure was associated with a brittle black skin 1-2mm in depth which showed a drop in fluorine (F) level at the surface to 19% (from 54% for deplasticised material) to 46% F at a depth of 300µm. Allied to this were reductions in crystallinity levels (40% from *ca* 46%) after 4 weeks at 120C together with dramatic changes in the molecular weight distribution (a description of molecular weights and their distribution relating to polymers being given in Appendix 1). After this ageing, the weight average molecular weight had increased nearly 10 fold and the z average by 3 or 4 times (Figures 2 and 3), mainly due to a large rise in the percentage of molecules with molecular weight greater than 10⁶. This indicates that considerable

crosslinking had occurred in the polymer due to the ageing. There was also evidence (from the shape of Figure 3) that some lower molecular weight species had formed, probably by chain scission. Including all samples again, after 2 weeks, crack growth resistance was rather low but it increased somewhat as exposure time increased to 4 and 6 weeks.

140C exposures

Increasing the temperature of exposure to 140C again caused the modulus to decrease (as at 100C) uniformly over the range 3 to 8 days and then again to increase as exposure duration increased through 2 and 4 weeks. Crack growth resistance was low after 3 days but then generally increased with exposure time (after ageing up to 4 weeks), after which crack growth resistance was above the unaged value (at the same level as that after 6 months/100C ageing). No darkening was observed on those samples only aged for days, but some discoloration was evident after 4 weeks.

General

Various of the properties have been plotted against time for each of the three ageing temperatures. By then choosing a common feature, for each temperature, the reciprocal of the time to reach it (a rate) for each temperature has been used to develop Arrhenius plots, albeit only for three temperatures. Figure 4(a) concerns modulus, specifically the time during initial stages to lose 4% of modulus.. Figure 4(b) shows two plots, again for modulus, for (i) the time to the minimum, (ii) the time from zero to reach a 10% increase above the minimum. Reasonable straight lines were obtained, the worst scatter arising for the last-named.

Figures 5(a) and 5(b) show the analogous plots for crack growth resistance, except that a 25% increase above minimum was used where appropriate in this case. Acceptable lines were obtained. Plots of the exposure time to reduce methane permeation coefficient to $0.06 \times 10^{-6} \text{ cm}^2/\text{s/atm}$ from the original unaged value of $0.3 \times 10^{-6} \text{ cm}^2/\text{s/atm}$ were similarly obtained and converted into the Arrhenius-type plot shown in Figure 6. At each temperature, this low permeation rate had only been attained well after modulus and crack growth resistance had passed their minima.

Activation energies E_a for the various plots are tabulated below.

<u>Property</u>	<u>Ea values (kcal/mole)</u>		
	<u>Initial stages</u>	<u>Time to minimum</u>	<u>Later stages</u>
Modulus	12.8	12.6	19.1
Crack growth resistance	24.5	21.3	21.3
HP methane permeation	-	-	13

Implications from the high crack growth resistance E_a data are that chemical changes apply throughout for properties governed by changes in the nature of the amorphous region. Modulus changes are governed by physical factors such as crystallisation levels, which (Table 1) exhibit minima generally coinciding with the modulus minima - some recrystallisation apparently occurs during later stages of the exposures. The high modulus-based E_a value at these later stages could reflect an interdependence of deplasticisation - only now beginning to dominate over the earlier softening effect of

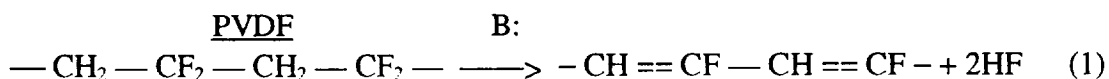
gas ingress (now at a constant level) - and crystallisation (see equivalent Tefzel report CAPP/M.13 Rev A for comments on interdependent factors).

The diagnostic methane permeation coefficient E_a value of 13 kcal/mole indicates that this property is largely governed by deplasticisation, TRI measuring 12.3 kcal/mole for the process itself.

A detailed examination of Table 1 shows that the 4 week/120C result, emanating from Batch 2, was quite different from other data obtained, as already described. Tensile failure was of a partly brittle mode, with ultimate strain at 16% - *much* lower than any other value, and only 4% greater than yield strain. Possible reasons for the different behaviour are discussed at the end of the 'Mechanisms' section (3.1.1). However, the view now is that such behaviour is the exception rather than the rule. (Other samples from Batch 2 were by coincidence employed with other fluids, some non-hostile e.g. Fluid B, where the main changes observed involved deplasticisation¹, and one sample for Fluid G - see later).

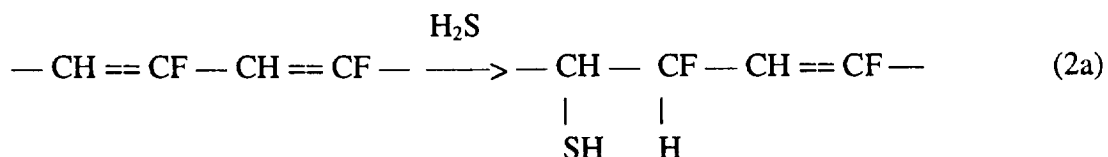
3.1.1 Mechanisms

A range of chemical reactions is possible: those proposed by project members are listed below. The darkening of material is characteristic of the formation of conjugated bonds *i.e.* unsaturated or carbon to carbon double bonds, specifically where the double bonds alternate with single bonds along the carbon backbone of the molecule. The presence of carbon to carbon double bonds is indicative of loss of HF from the carbon chain caused by reaction with the amine (shown below as a base B:). This is sufficient on its own to cause significant degradation, and proceeds as follows:-



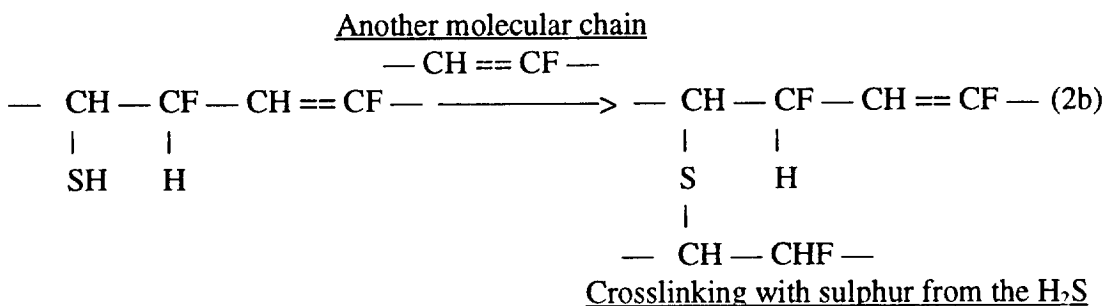
Reaction 1 is base-catalysed dehydrohalogenation (by an E2 mechanism) as occurs in many organic hydrogen halides, and is possible here due to the activation of the CH bonds by the adjacent CF_2 groups. If this reaction were reversible, the forward reaction could be favoured by a subsequent reaction such as that below (2a), and by escape or perhaps by removal of HF (cf reaction 1a, but more doubtful as amine alone, Fluid H, did not cause darkening).

The second reaction cited involves the H_2S in Fluid F, which reacts in two stages with the product from reaction 1 to form crosslinks. The first stage is summarised by:

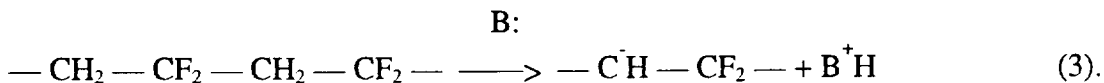


Normally this reaction occurs by a free radical (anti-Markownikoff) mechanism (initiated by ultra violet radiation or the presence of a chemical initiator). In the present case, the initiator might derive from B:

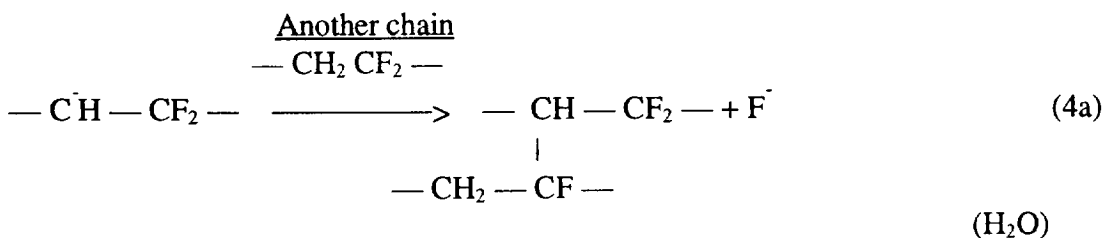
Then the second stage is electrophilic addition:



An alternative crosslink mechanism not involving sulphur may not require an initial unsaturation step, but still needs suitable activation (by the base B:)



Then:

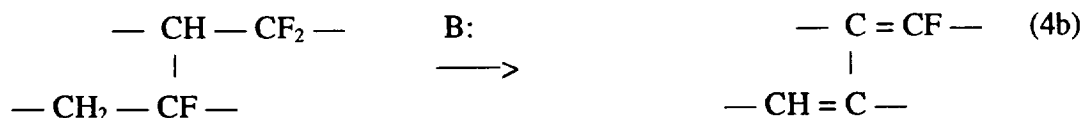


(H₂O)



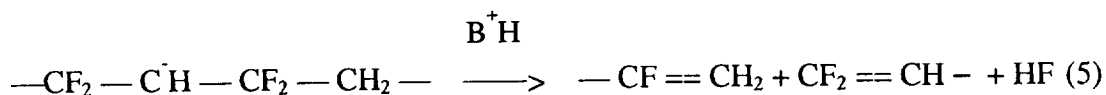
Crosslinking without S

This ionic mechanism probably occurs more readily when water is present. Further reaction with base may occur subsequently to yield a conjugated (black) structure for this crosslinked system that does not involve S:



which taken together with the possibility of the crosslink being a double bond could induce further brittleness.

However, instead of progressing to a crosslinking stage, the product from reaction 3 may further react together to yield *smaller* molecules:



chain cleavage or scission

Whether crosslinking or scission occurs depends on whether or not molecular conformations are such that equation 4a proceeds before B^+H performs its attack, and/or whether HF can be removed.

For samples other than the 4 week/120C sample from batch 2, evidence of just a little chemical change is shown from Table 2 analytical data. From GPC results, reaction 5 has apparently occurred relatively early in the exposures, which infers that reaction 3 had already occurred: GS/MS data support this as the observed acid degradation product from the plasticiser probably arose from an HF catalysed hydrolysis, and (in the absence of sulphur crosslinking) HF is most likely to arise from reaction 5. At this stage, crosslinking reaction 4a was presumably less favoured. After longer times no GPC data are available, but the variously-derived activation energies (section 3.1) each indicate the relevance of chemical mechanisms here, so that now reaction 4a and, on occasions, reaction 4b, are more involved. Nevertheless the total chemical change is not greater after all exposures conducted for Coflon samples from Batches 1, 3 and 4.

For the Batch 2 sample, the story is apparently quite different. Build-up of unsaturation and crosslinks caused stiffening of the polymer by reducing the amount of molecular movement possible. As well as those above, reactions 1 to 2b are probably also heavily involved. To support this mechanism, ESCA, SEM, X-ray Fluorescence and Elemental Analysis all show tremendous loss of fluorine at the sample surface (*i.e.* dehydrofluorination has occurred). GPC shows large increases in molecular weight at the high end of the distribution which will be due to crosslinking, and at the low end which probably results from chain scission. Amine and probably H_2S are needed to fit these observations a) to unsaturate and then b) crosslink. With the same batch, fluids with just H_2S present (D and E) caused no discoloration or drop in fluorine level, and fluids with neither amine or H_2S (B and C) also caused no visible or chemical change. Fluid (vapour) with just amine present (H) showed a surface colour change to yellow but no loss of fluorine whilst J (liquid) showed a more severe blackening again. Hence reactions 1, 2a and 2b are likely to be strong contributors to the considerable Batch 2 Coflon ageing observed in Fluid F.

The obvious question concerns the difference between Batch 2 data and the remainder. To lead to one possible reason, it has been observed in the project that (1) Batch 2 was much easier to deplasticise than later batches, and (2) crystallinity levels can vary from 9% to 37% for different regions across the 6mm section of extruded Coflon (TRI localised X-ray diffraction measurements). The two observations may be interlinked - the degree of crystallinity in surface regions could control deplasticisation rate. The significance of this regarding ageing concerns the relative mobility, conformations and

locations of PVDF chains when plasticiser is or is not present. Clearly, degradation reactions can occur singly, i.e. independent of chain locations, but for crosslinking to occur, chains have to be close enough: whether plasticiser is present or not could be significant in deciding the proximity of the chains, and hence the subsequent reactions which occur. Alternatively plasticiser might prevent H_2S from forming free radicals necessary for the anti-Markownikoff mechanisms associated with reaction 2(a).

3.1.2 Conclusions for Fluid F

Possible reactions involving Fluid F (containing H_2S , amine, and water) have been listed. It is considered that the amine alone may be capable of causing some chemical degradation. However, the H_2S may cause further deterioration. Firstly the amine causes conjugated unsaturation by the removal of HF. Degradation then proceeds via a further reaction, either by chain scission or by crosslinking with the H_2S , involving the sulphur and conjugated double bonds, to yield a stable or energetically favourable product. However, it is likely that this is an aggressive form of crosslinking not always met. Another, slower, non-sulphur, ionic, crosslinking process may be more common. For example, ageing-induced darkening of specimens is due to unsaturation because of conjugation. As the 140C aged samples did not darken (but had degraded), they may have crosslinked by the alternative mechanism not involving sulphur.

At 100C, 120C and 140C, after initially decreasing, tensile modulus increases. The exact changes presumably depend on a combination of plasticisation by gas ingress, dibutyl sebacate deplasticisation, loss of crystallinity and then recrystallisation and chemical reaction. For one Coflon batch in particular ("Batch 2"), build-up of crosslinks and unsaturation increased stiffness by reducing molecular motions. For all samples, initially, chain scission decreases stiffness.

Crack growth rate was greatly increased after initial ageing but then tended to decrease with increasing duration of exposure. More reliable comparisons were made possible by defining crack growth resistance, which is a J factor applying to a particular crack growth rate, and responds inversely to changes in crack growth rate. This term increased with deplasticisation, decreased with initial ageing and then increased after longer exposures. Good Arrhenius plots have been obtained from these data, with E_a values suggesting dependency on chemical reactions. It is likely that crack growth fatigue testing is dominated by amorphous regions of the Coflon.

According to other E_a information, changes in HP methane permeation after ageing tended to reflect loss of plasticiser rather than any change due to chemical or morphological effects.

For 4 week/120C aged samples from Batch 2 only, GPC showed changes in molecular weight distribution at the high end, indicative of crosslinking. In addition, study of the split peak produced (Figure 3) shows that some chain scission has also occurred. ESCA, X-ray Fluorescence and Elemental Analysis all showed tremendous loss of fluorine (F) at sample surfaces due to dehydrofluorination. X-ray diffraction showed crystallinity losses during ageing, to indicate a possible linkage with dehydrofluorination. For this batch, it is likely that the S-crosslinking route applied: even so, the amount of S present would probably be undetectable by analysis. However, all the other batches of Coflon displayed less severe signs of ageing. It is

suggested that plasticiser may interact with a Fluid F constituent either physically or chemically to delay or alter the effects of ageing/conjugation, depending on the amount of constituent or plasticiser present initially: the content of the latter, and how easily it is lost, could depend strongly on local crystallinity levels across the Coflon section (and especially at the surface). H_2S might be absorbed by plasticiser via a free radical mechanism. To support this, GC/MS analysis has listed some S-containing organic compounds as perhaps being in the plasticiser-extract after Fluid F ageing.

Samples exposed to water and amine (Fluid J) changed colour to black, whereas samples exposed to CH_4 / CO_2 / H_2O and amine changed colour on the surface to yellow, with no loss of fluorine (F) recorded. Similarly CH_4 / CO_2 / H_2S (no amine) with or without H_2O gave no discoloration or change in F level. These observations illustrate the relative stability of PVDF, the amine concentration dependence of degradation, the possibility of synergism between H_2S and amine attack, and the fact that water might enhance the alternative (ionic) slow crosslinking process.

The only apparent correlations indicated thus far are between crack growth resistance and crystallinity, and with fluorine content when hostile attack has occurred. Where only small differences between yield and ultimate strains unexpectedly occur, this is indicative of the onset of ageing-induced brittle failure.

3.2 Fluid A (methanol)

Exposures were carried out at both 5000psi and vapour pressure with the specimens in the liquid. Table 2 summarises the property and limited appropriate analytical results for these Fluid A exposures at several temperatures and durations. The previous comment on unaged batch-to-batch variations again applies. This table again illustrates two sets of control data, showing, for instance, the higher modulus of deplasticised PVDF. After 1-2 weeks at $140^\circ C$ and vapour pressure, catastrophic deterioration has been reported². However, some data were obtained at less severe conditions.

Ageing at $140^\circ C$ and 5kpsi exhibits swinging changes in modulus. After *ca* 7 days, a considerable increase suggested some plasticiser loss by leaching. This was apparently faster than replasticisation by methanol ingress, which however then occurred, because after 14 days the tensile modulus had dropped significantly towards half the unaged value and the ultimate strength decreased. In contrast, at $140^\circ C$ and *vapour pressure*, after only 4.5 hours modulus was below one third of the unaged value: this had decreased further after 18 hours (and the specimen deteriorated significantly in the days following). After exposures at $100^\circ C$ and $120^\circ C$, modulus had again been reduced by ~50%, but there was less of a time effect. Other tensile properties were not affected to a great degree, except that, after 18 hours at $140^\circ C$, stress/strength values had decreased significantly, presumably signifying the onset of the severe deterioration stage. There was no evidence of brittle behaviour, both visually and from strain values.

Fracture toughness showed a decrease after the 7 day $140^\circ C$ exposure compared with 100% deplasticised material. Crack growth rate after a 5 day/ $120^\circ C$ exposure was

between the unaged and deplasticised values, and after longer times and temperatures was now very high. Some of these values were influenced strongly by single points on the plots. Crack growth resistance values reflected these changes more realistically from the plots and, unlike the rate measurements, gave a comparison at the same condition. At 120C, after 5 days the resistance was at the unaged level but after 126 days it was considerably reduced. Similarly, long times at 100C gave reduced crack growth resistance. At 130C, the resistance was reduced after a few hours only, and at longer times, or for all 140C exposures, no fatigue crack growth tests could be performed because of the deterioration.

Crystallinity levels of three vapour pressure aged samples at 100C and 120C were much reduced (but stable) compared with the deplasticised value, but for the 140C aged deteriorated 'crumb', ironically the reduction in crystallinity was less (see Table 2 footnote); perhaps PVDF had completely dissolved in the methanol when hot and then recrystallised to a crumb on cooling.

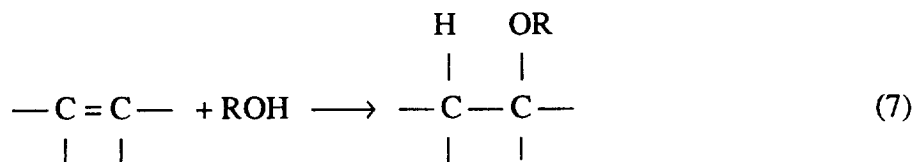
3.2.1 Mechanisms

A large proportion of hot methanol deterioration (especially at 140C) is physico-chemical: to support this, the MWD of fully-deteriorated Coflon 'crumb' after 13 days at 140C in methanol (see footnote, Table 2) was not too dissimilar from the unaged value in Table 1. For any chemical reactions which do occur, any double-bond formation would be with methanol acting as a weak base in the reaction shown by equation 6, which is PVDF behaving as a hydrogen halide and reacting with methanol by an SN2 mechanism:



Production of CH₃F in this way might explain the bubbles seen during some of the methanol ageing tests as mentioned elsewhere². However, very little colour change was noted before samples disintegrated, suggesting that double bond formation was not the primary reaction.

Any crosslinking that might occur would be by reaction 4a, (following 3) and any scission by reaction 5. A side reaction after equation 6 could be base catalysed addition of primary alcohols to alkenes:



which would cause equation 6 to proceed, but not cause crosslinking: the -OR groups would probably be detectable (e.g. FTIR).

3.2.2 Conclusions for Fluid A

Material deterioration which occurred when hot, and at vapour pressure especially, has a high physicochemical contribution. As a consequence, both crack growth resistance (and rate) and tensile modulus diminished significantly.

Crystallinity level was diminished by long exposures at 120C, but it was decreased less at 140C after 13 days. It seems that chemical attack occurs at 120C, but at 140C it is swamped by the physico-chemical contribution. Crack growth testing itself cannot differentiate between the two; contributions from tensile testing are required.

The physico-chemical effect is much diminished at 5000psi.

Comparisons are not possible between analytical and mechanical property results because tests were frequently not performed at the same conditions.

3.3 Fluid G (methanol + amine)

This fluid comprises methanol plus 1% of ethylene diamine: all exposures were at 5000psi, with testpieces immersed in liquid.

The relatively-few results obtained with analytical data for comparison are shown in Table 3: CAPP/M.12 Rev A includes a few more tensile data than those shown in this table, but these were not included herein because no other data existed for comparisons. The tensile modulus after the 4 week/120C exposure was low, similar to that after long methanol exposures. However, in this case, the failure mode was completely brittle, as evidenced by a difference of only 0.5% between yield and ultimate strains (these being low also). The same effect showed at even lower modulus after 6 weeks, (and for the extra data in CAPP/M.12 Rev A). The appearance of the specimen was cracked all over its surface and small pieces could easily be chipped off. A chemically-induced change was strongly indicated.

A diffusion-type profile of strongly decreasing F content towards the surface was measured. The methanol probably acted as a carrier for the amine. The chemical attack occurred irrespective of which Coflon batch was being used (occurring on Batch 2 and other batches). No work was performed at 140°C; it is considered that the combination of this strong chemical attack and the physico-chemical attack at 140°C which occurs with methanol alone (cf Fluid A data) would lead to deterioration at an unacceptably fast rate.

Crystallinity was much reduced. The Mz portion of the MWD was very high (the highest value measured to date in this work), implying excessive crosslinking which could only occur via reaction 5b. However, chain scission has also occurred, which could account for the surprisingly low modulus associated with brittle failure.

HP methane permeation coefficient has reduced after the ageing period compared with the unaged value, but shows no difference from the deplasticised value. Few tests were conducted because the surface cracks affected the measurements.

No crack growth fatigue data have been obtained due to the overall cracked and crumbly nature of the samples after ageing in Fluid G.

The only Arrhenius plot obtainable was for initial modulus decrease (Figure 7), which gave an E_a of 10.6 kcal/mole (a value associated with physical factors such as crystallisation level as discussed for Fluid F ageing).

3.3.1 Mechanisms

Those reactions referred to for amine and 100% methanol (i.e. equations 1, 3, 4a, 4b, and 5, 6 and 7) would again apply here. However, the presence of the excess amine base has apparently caused forward reactions to proceed at speed: the catalytic effect of this base for equations 3, 4a and 4b is thus indicated. In summary, the mechanism was apparently crosslinking and dehydrofluorination possibly followed by the base-catalysed addition of methanol to double bonds so formed.

3.3.2 Conclusions for Fluid G

Fluid ingress resulted in ageing giving a good diffusion profile according to fluorine content values: also, crystallinity was much reduced.

Virtually all exposures (except the shortest low temperature one) gave brittle tensile failures due to excessive crosslinking, but the presence of low molecular weight fractions (scission) means that modulus is also low. The resulting conclusion that ageing was chemical is supported by change in MWD, appearance, and the tiny difference of 0.5% between tensile yield and ultimate strain. Although the modulus-derived E_a was at a physical level (see above), it is highly probable that an E_a derived from crack growth resistances at different temperatures (had these tests been possible) would have been high, depicting chemical means (as for Fluid F). Unlike tensile testing, this test mode is thought to be governed by the amorphous region, the region which is affected directly by any chemical attack.

Permeation data showed the same reduction from unaged values as that obtained for deplasticised samples.

4 FURTHER DISCUSSION

Early in the project, to explain the consequences and data from the first exposures in Fluid F mixtures (employing already-aged Coflon permeation samples donated by Exxon Production Research), the need for synergism between certain chemical reactions, which in the extreme could result in affected PVDF regions becoming in essence crosslinked polyethylene, was proposed. Certain chemical reactions leading to conjugation and crosslinking of this type have been suggested by TRI, and their analytical data support the proposed general mechanism for what has now been termed 'hostile attack'. It is now realised that the basic cause of attack is the amine which may cause both crosslinking and then conjugation (without S) on its own. Extra information from GPC measurements, indicating that chain scission also occurs, is most useful. In other words, a 'gentle' form of chemical ageing due to Fluid F can occur and is probably more common. For one batch - "Batch 2" - the hostile form of attack has been noted. As well as the basic non-S reactions, this probably involves H_2S and amine as originally suggested. The question then arises as to why the different modes exist. A reason for the difference in morphological terms has been

given. A poor batch could be detected by loss of tensile ultimate strain after 4 weeks at 120C in Fluid F.

For liquid exposures in 100% methanol, which is chemically-similar to PVDF, then liquid ingress into amorphous regions followed by stepwise detachment of surface molecular chains from crystallites is the likely mode of 'attack'. During the project, recrystallised PVDF (of normal crystallinity levels according to DSC) has been obtained from filtered solutions following 140C methanol exposures to prove how important this physicochemical process can be.

Liquids can also cause chemical attack (Fluids G and J). Aged samples were very brittle, shown by low tensile strains and moduli, a combination explicable by GPC data. Here, the non-S reactions discussed above have produced more hostile activity. One key reaction might be 6, producing water, to allow the ionic reactions 3 to 5 to occur; the extent of the reactions is probably governed by the fact that the amine is in a liquid phase (and hence relatively-concentrated) rather than in a vapour phase as with Fluid F.

High pressure gas permeation data have also shown trends, indicating how Arrhenius plots exist, but are tempered by pressure effects which diminish rates. Deplasticisation also reduces rates. This assessment has indicated that gas permeation rates are mainly governed by depasticisation only.

Regarding the mechanical tests, the best result for the project would be to have one test which is responsive to all ageing-induced changes and which accurately represents the material's characteristics in any environment. The results indicate that this goal is impossible to attain. Crack growth during fatigue testing of samples at service conditions represents the most fundamental method of representing flexible pipe performance, providing that a service-related J value is applied. In reality, two reasons why this is difficult are:

- 1 the tests would be very long.
- 2 the wide spread of crack growth rate values possible at low J values (which would apply) would make assessments difficult.

If these problems could be removed, then fatigue testing after appropriate ageing at service conditions would determine whether the material was still suitable for pipe service, irrespective of whether it possessed a brittle skin, or low molecular weight polymer, etc. More practically, performing the test at higher J values overcomes the problem in testing terms by accelerating the tests so that shorter times can be used, and by moving to the steeper portion of the crack growth rate versus J plots. For the second point, even then, wide variations in individual rates can occur but the steepness of the plots in this region means that by using the crack growth resistance concept as defined, the effect of these variations is minimised. Crack growth resistance has been used successfully to obtain Arrhenius plots for Fluid F ageing. The choice of the crack growth rate value for defining the resistance is empirical, for convenience only, but should be a little greater than maximum rates measured in the low-J, near-horizontal, portion of the crack growth versus J plot.

By using this approach, the fatigue crack growth test is a materials rather than a performance test. From the present assessment, its data relate to the chemical ageing of the amorphous region (the crack tip might be visualised as advancing slowly between crystalline regions, moving them aside as well as eventually fracturing some of them). Tensile strains reflect the onset of ageing-induced brittleness. However, in contrast, as PVDF is a high-crystallinity polymer, tensile modulus measurements are apparently not affected by amorphous regions - instead, they strongly reflect changes in crystallinity or plasticiser level etc. Hence the test type should be chosen with a particular objective in view. In the present work, a good balance has been achieved by using both of these tests.

5 GENERAL CONCLUSIONS

On the evidence available, the basic material test measurement for following chemical ageing is fatigue crack growth resistance, obtained using compact tension testpieces. However, to avoid data scatter and to accelerate the test, higher J values than apply in flexible pipe service are required. The empirical concept of crack growth resistance gives a useful overall quantification of the data. Tensile data can provide added information:

- low strain values can indicate brittle failure
- modulus decreases can indicate physico-chemical fluid absorption or loss of crystallinity (to soften the polymer), or deplasticisation (to stiffen it).
- Property changes may not be linear with time.
- With Fluid F exposure, a correlation is indicated (although not without some inconsistency) between crack growth resistance, crystallinity level and fluorine content. Interbatch variations can complicate matters: reasons are proposed for the occasions when considerable ageing occurs to give brittle failures.
- Data from various fluids detailed where modulus changes might be informative:
 - (General), deplasticisation increases modulus
 - (Fluid A), physico-chemical absorption of a liquid may reduce modulus sequentially, as well as decrease crack resistance similarly
 - (Fluid F), as ageing time progresses, both moduli and crystallinity levels pass through minima
 - (Fluid G), if chain scission occurs concurrently with crosslinking, a low modulus might be associated with brittle failure
- Mechanisms proposed in the project for the various types of deterioration observed have been supported by analytical data.
- Various caveats have been recorded which must be heeded when making comparisons.

ACKNOWLEDGEMENTS

This report is a resumé of data and ideas from all members of the CAPP project team at MERL and TRI. Sources of information are the CAPP technical reports, progress reports, meeting notes and personal discussions.

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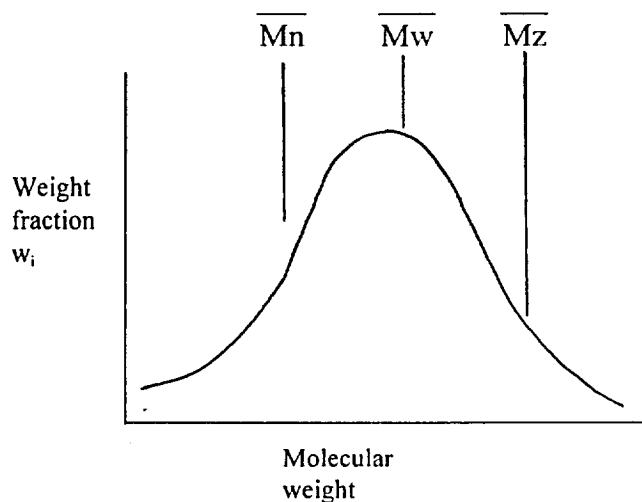
- 1 R P Campion, M Samulak, A Stevenson and G J Morgan, Proc Conf "Oilfield Engineering with Polymers" (London), publ. MERL, page 60 (October 1996).
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APPENDIX 1

Molecular weights (masses) of polymers

A polymer does not consist of molecules all the same size (although they are all large) but rather as an assembly of molecules with a distribution of sizes *i.e.* polydispersity. Molecular size is therefore expressed in terms of molecular weight averages.

Consider a simple molecular weight distribution which represents the weight fraction w_i of molecules having relative molecular masses M_i . It is possible to define several useful average values: their approximate positions are shown in the sketch.



On the basis of the number of molecules N_i of a particular size M_i we obtain the Number Average Molecular Weight \bar{M}_n , whereas averaging on the basis of weight fraction w_i of molecules of a given mass M_i leads to the definition of Weight Average Molecular Weight \bar{M}_w . Then

$$\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i} \quad \text{and} \quad \bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

\bar{M}_w reflects more accurately mechanical properties and melt viscosity. To explain physical properties fully, knowledge of the complete molecular weight distribution (MWD) is informative. To determine this, the width of the curve in the figure can be quantified by the ratio \bar{M}_w / \bar{M}_n . Typical values prepared by TRI as guidelines are:

	\bar{M}_w / \bar{M}_n
Very narrow	<1.2
Narrow	1.2 - 2
Medium	2 - 4
Broad	4 - 10
Very broad	>10

NB Tails on the low M side of the distribution will affect \bar{M}_n most, on the high side will affect \bar{M}_z most, and \bar{M}_w is near distribution centre (not necessarily at the peak).

If for any reason (e.g. effects of ageing) higher molecular weights are important, then a convenient and useful definition of an average value is given by the “z-average”, so that

$$\overline{M}_z = \frac{\sum N_i M_i^3}{\sum N_i M_i^2}$$

Thus $\overline{M}_z / \overline{M}_n$ can be used as an alternative means of quantifying MWD.

In this project, examples have been found after ageing where a second peak occurs after ageing, at high molecular weights. Then the role of \overline{M}_z (or $\overline{M}_z / \overline{M}_n$) becomes informative. This is because crosslinking has extended the high M side. In addition, chain scission might have extended the low M side, at the expense of medium M molecules. It has been observed that, under these conditions, it is better to study and compare the shapes of the peaks to determine whether one sample possesses more low M species than another; comparison of \overline{M}_n values can be misleading here.

TABLE 1: COFLON AGED IN FLUID F ($\text{CH}_4/\text{CO}_2/\text{H}_2\text{S}/\text{H}_2\text{O} + 1\%$ ethylene diamine) AT 5000 psi

Properties measured at 23°C unless indicated otherwise

Sample and aging history	Modulus MPa	Yield strain %	Yield stress MPa	Ultimate strain %	Ultimate strength MPa	Mode of fracture	Fracture toughness kJ/m^2	70°C Crack growth		Stress relaxation rate % per decade	Permeation coefficient $\text{CH}_4/140^\circ\text{C}/5\text{kpsi}$ $\text{cm}^2/\text{s}/\text{atm} \times 10^{-6}$	Crystallinity (X-ray diffr'n) %	Mol. wt distribution	Visual appearance and other results, analyses and observations
								rate* ($J=2$ unless+) nm/c	resistance (J for $10\text{nm}/\text{c}$) kJ/m^2					
aged	¹ 800	15	35	58	35	Ductile	48 ($c=2$)	150*	3.2	13.3 (11.5)	0.3	41.5	Mn=81,700 Mw=538,900 Mz=3,217,000	Off-white, translucent 48% F
	² 760	16	36	90	36			0.4						
	³ 670	17	37	100	37									
	⁴ 750	15	36	90	36									
elastified	¹ 1,450	9.5	47	29	31	Ductile	60 ($c=2$)	8* ~0.1	4.1	12.7	0.05	40	Mn=171,265 Mw=538,897 Mz=1,067,315	Light brown 10% loss in wt 20% loss in vol 54% F
1 month 100°C	³ 609	19	38	80	38	Ductile			2.6			27	Mn=85,600 Mw=332,800 Mz=784,400	
1 month 100°C	³ 627	22	38	91	38	Ductile		>10,000	2.4		0.11	39, 43	Mn=105,800 Mw=281,800 Mz=503,100	Some discoloration, dark patches and edges
1 month 100°C	³ 685	45	38	71	38	Ductile			3.4		0.04	42	Mn=177,880 Mw=549,827 Mz=1,084,282	57% F
1 week 120°C	⁴ 718	17	36	61	36	Ductile			2.2					
1 week 120°C	³ 711	17	38	72	38	Ductile		20	1.8		0.08	35, 25	Mn=152,905 Mw=534,361 Mz=1,080,943	Some discoloration, dark patches and edges 57% F
1 week 120°C	⁴ 748	25	37	74	37	Ductile						41, 40	Mn=173,803 Mw=539,103 Mz=1,073,977	57% F
1 week 120°C	² 896	12	38	16	38	Partly brittle		1,500* 1.5	2.4	12.9	0.12	40 (29)†	Mn=108,900 Mw=4,491,000 Mz=11,840,000	Brittle black skin (1-2mm), white core Surface 19% F to 46% F at 300µm
1 week 120°C	⁴ 824	38	38	69	38	Ductile			2.2		0.05			

Continues on to 2nd page

TABLE 1 (cont)

Sample and aging history	Modulus	Yield strain	Yield stress	Ultimate strain	Ultimate strength	Mode of fracture	Fracture toughness	70°C Crack growth	Stress relaxation rate	Permeation coefficient	Crystallinity (X-ray diff'n)	Mol. wt distribution	Visual appearance and other results, analyses and observations
Days 140°C	³ 621	20	36	83	37	Ductile		>100,000	1.5		31, 26	Mn=177,460 Mw=536,509 Mz=1,062,095	Off-white discoloration 56% F
Days 140°C	³ 562	21	36	91	36	Ductile			2.0		27, 28	Mn=173,3290 Mw=534,908 Mz=1,059,213	Off-white 56% F
Days 140°C	³ 556	25	35	94	35	Ductile		300	1.8	0.16	34, 29	Mn=170,504 Mw=532,717 Mz=1,052,564	Off-white 56% F
Weeks 140°C	⁴ 901	16	38	60	38	Ductile					39, 29		
Weeks 140°C	⁴ 845	25	37	67	38	Ductile				0.06	37		

NB: Different batches of Coflon have been tested and have different initial moduli.

¹ = batch 1

² = batch 2

³ = batch 3

⁴ = batch 4

* All obtained by extrapolation except the 2 week/120°C result.

† Value in parentheses is % crystallinity at sample outer surface.

+ J= 4kJ/m²

TABLE 2: COFLON AGED IN FLUID A (methanol)

Properties measured at 23°C unless indicated otherwise

Sample and ageing history	Modulus	Yield strain	Yield stress	Ultimate strain	Ultimate strength	Mode of fracture	Fracture toughness (c = 2)	70°C Crack growth		Crystallinity (X-ray diff'n)	Visual appearance and other results analyses and observations
	MPa	%	MPa	%	MPa		kJ/m ²	rate (J=4) nm/c	resistance (J for 10nm/c) kJ/m ²	%	
Unaged	¹ 800 ² 760 ³ 670	15 16 17	35 36 37	58 90 100	35 36 37	Ductile	48	150	3.1	41.5	Off-white, translucent 48% F (MWD given in Table 1)
Deplasticized	¹ 1,450	9.5	47	29	31	Ductile	60	8	4.1	40	Light brown, 10% loss in wt 20% loss in vol. 54% F (MWD given in Table 1)
7-8 days 140°C, 5 kpsi	¹ 1150 [†]	10 [†]	50 [†]	22 [†]	34 [†]	Ductile	45 [†]				Yellow
14 days 140°C, 5 kpsi	¹ 483	34	30	64	26	Ductile					Translucent brown, dark central region. Had shrunk.
14 days 140°C, 5kpsi + 7.5% strain	¹ 417	41	30	93	23	Ductile					"
79 days 100°C, vap.pr.	¹ 509	35	33	66	33	Ductile		(1000) J=2	1.8		Yellow
126 days 100°C, vap.pr.	¹ 479	24	34	59	35	Ductile		15 J=2	1.9	29	Light brown Mn=101,900 Mw=350,300 Mz=762,800
217 days 100°C, vap.pr.	¹ 476	22	33	78	34	Ductile					
18 hours 120°C, vap.pr.	¹ 427	35	30	110	24	Ductile					Little noticeable change
5 days 120°C, vap.pr.	¹ 435	30	32	99	26	Ductile		30	3.1		Light yellow
22 days 120°C, vap.pr.	¹ 460	29	32	82	32	Ductile				25.5	Yellow
79 days 120°C, vap.pr.	¹ 424	37	33	84	33	Ductile					Light brown
126 days 120°C, vap.pr.	¹ 422	31	32	75	32	Ductile		200 J=2	1.7	26	Mid brown Mn=115,400 Mw=379,600 Mz=814,500
217 days 120°C, vap.pr.	¹ 403	26	29	69	30	Ductile					
4.5 hours 130°C, vap.pr.	¹ 373	35	28	112	24	Ductile		500 J=3	2.0		Yellow
4.5 hours 140°C, vap.pr.	¹ 276	28	22	36	19	Ductile					Yellow
18 hours 140°C, vap.pr.	¹ 254	30	18	110	18	Ductile					Yellow

NB: Different batches of Coflon have been tested and have different initial moduli.

¹= batch 1 ²= batch 2 ³= batch 3

[†] 3% strained + Value for both strained and unstrained.

Parentheses indicate extrapolated value

NOTE: The MWD for a 13 day/140°C/vapour pressure sample was Mn 92,900, Mw 636,100, Mz 2,060,000: its crystallinity level was 34%. Because the material had completely deteriorated, no other tests were possible.

TABLE 3: COFLON AGED IN FLUID G (methanol + amine) at 5000psi

Properties measured at 23°C unless otherwise indicated

Sample and ageing history	Modulus	Yield strain	Yield stress	Ultimate strain	Ultimate strength	Mode of fracture	Permeation coefficient	Crystallinity (X ray diffraction)	Mol. wt distribution	Visual appearance and other results, analyses and observations
	Mpa	%	MPa	%	MPa		cm ² /s/atm x10 ⁻⁶		MWD	
Unaged	¹ 800	15	35	58	35	Ductile	0.3	41.5	Mn=81,700 Mw=538,900 Mz=3,217,000	Off-white, translucent 48% F
	² 760	16	36	90	36					
	³ 670	17	37	100	37					
	⁴ 750	15	35	114	36					
Deplasticized	¹ 1450	9.5	47	29	31	Ductile	0.05	40	Mn=171,265 Mw=538,897 Mz=1,067,315	Light brown 10% loss in wt 20% loss in vol 54% F
2 weeks 65°C vapour pressure	⁴ 694	17	36	40	36			39		
2 weeks 120°C	⁴ 698	15	31	16.8	31	Totally brittle		32		Black all through Surface cracks
4 weeks 120°C	² 452	14	28	14.5	25	Totally brittle	0.05	11.5	Mn=44,300 Mw=3,742,000 Mz=143,940,000	Black all through Surface cracks Surface 12% F to 36% F at 300µm
6 weeks 120°C	⁴ 330	11	17	11	17	Ditto				

NB: Different batches of Coflon have been tested and have different initial moduli.

¹= batch 1 ²= batch 2 ³= batch 3 ⁴= batch 4

* Estimated: lower value is for Fluid E exposure associated with little MWD change, increased F, decreased C and O and no discoloration, and hence which reasonably caused deplasticization only, and higher figure is unaged value normalized for the loss of 11% (17 vol %) of dibutyl sebacate.

NOTE: Crack growth fatigue data were not obtained at the time Fluid G was introduced due to a lack of compact tension testpieces, and subsequently due to excessive surface cracking on these testpieces after the exposures.

crack growth

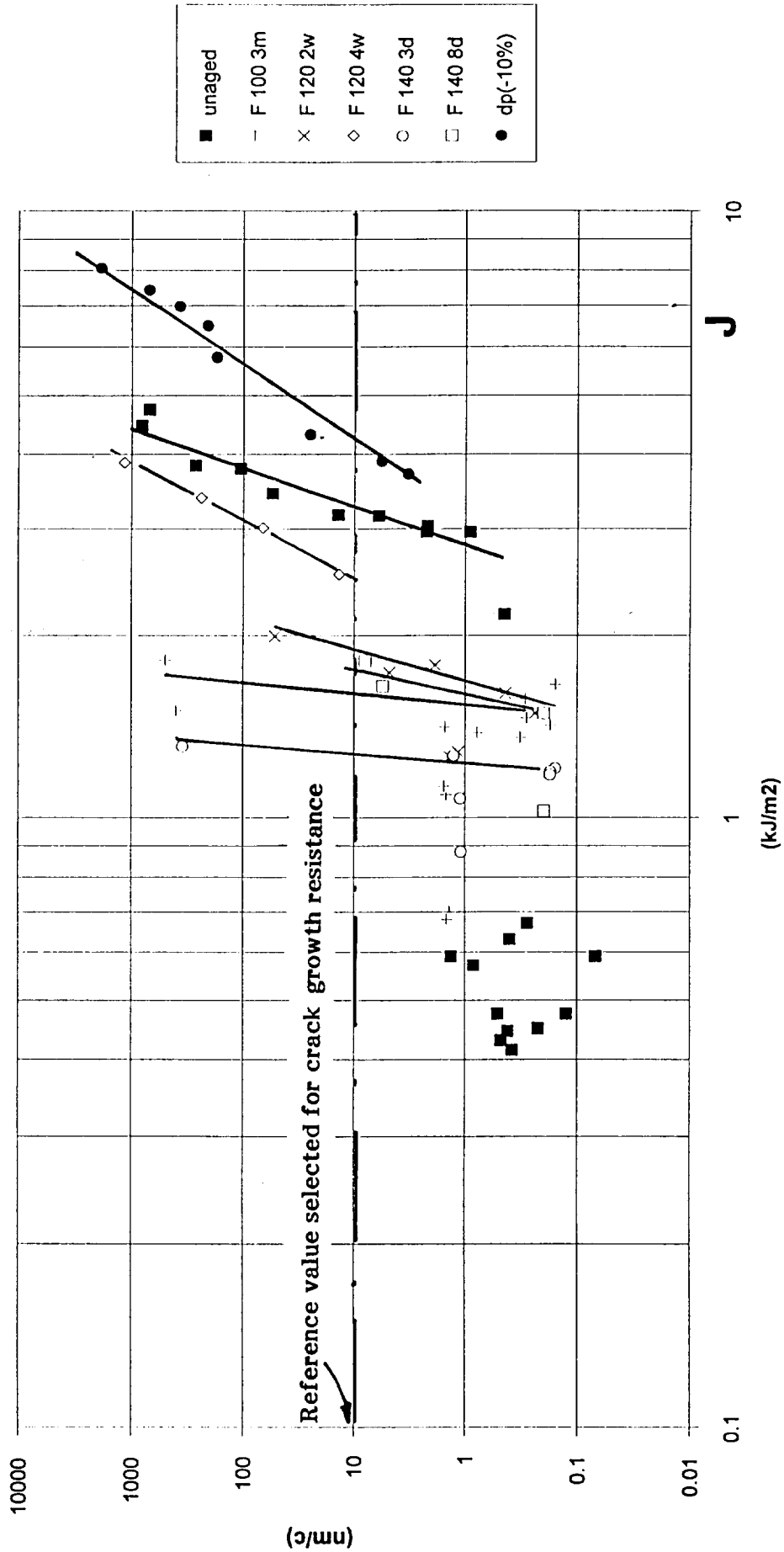


FIGURE 1 CT fatigue testing of Coflon after various Fluid F exposures

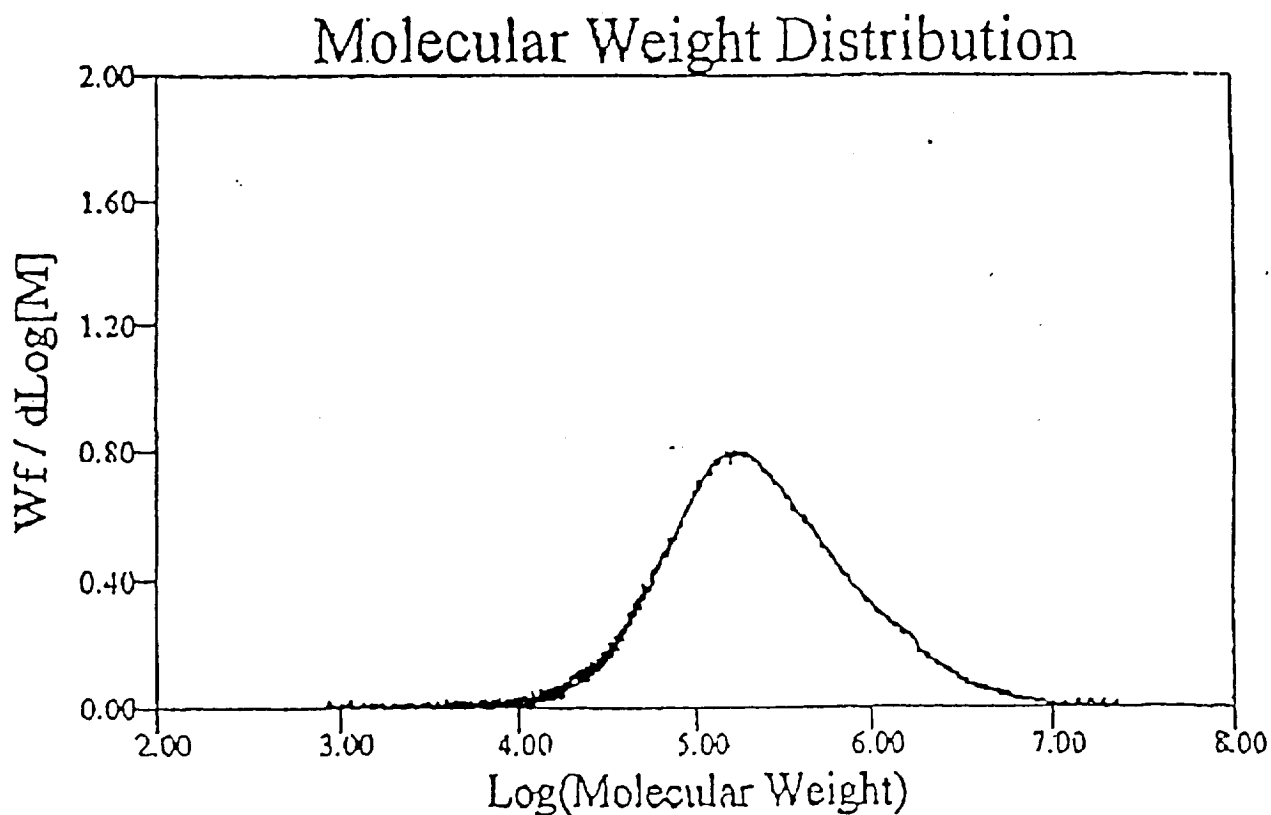


FIGURE 2 MWD for unaged Coflon PVDF

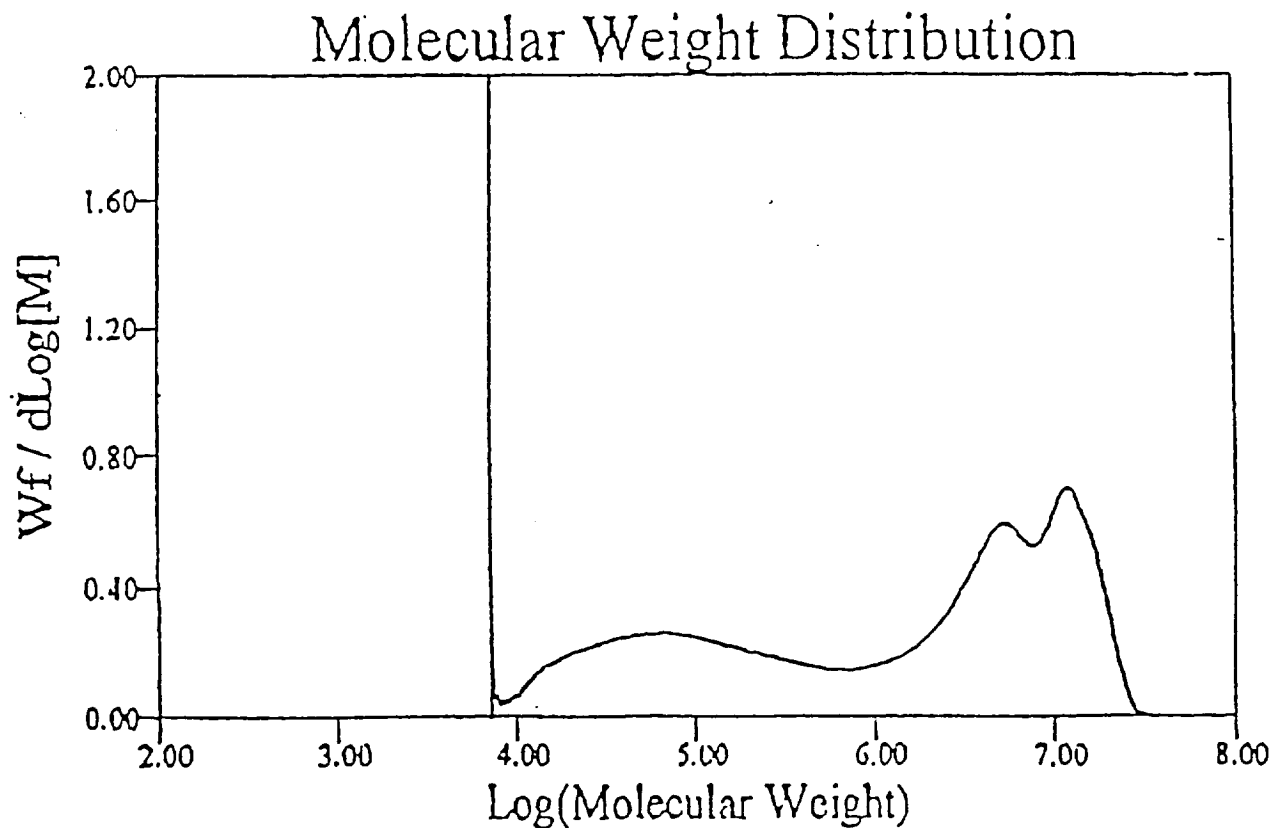


FIGURE 3 MWD for Coflon PVDF aged 4 weeks at 120°C in Fluid F at 5kpsi

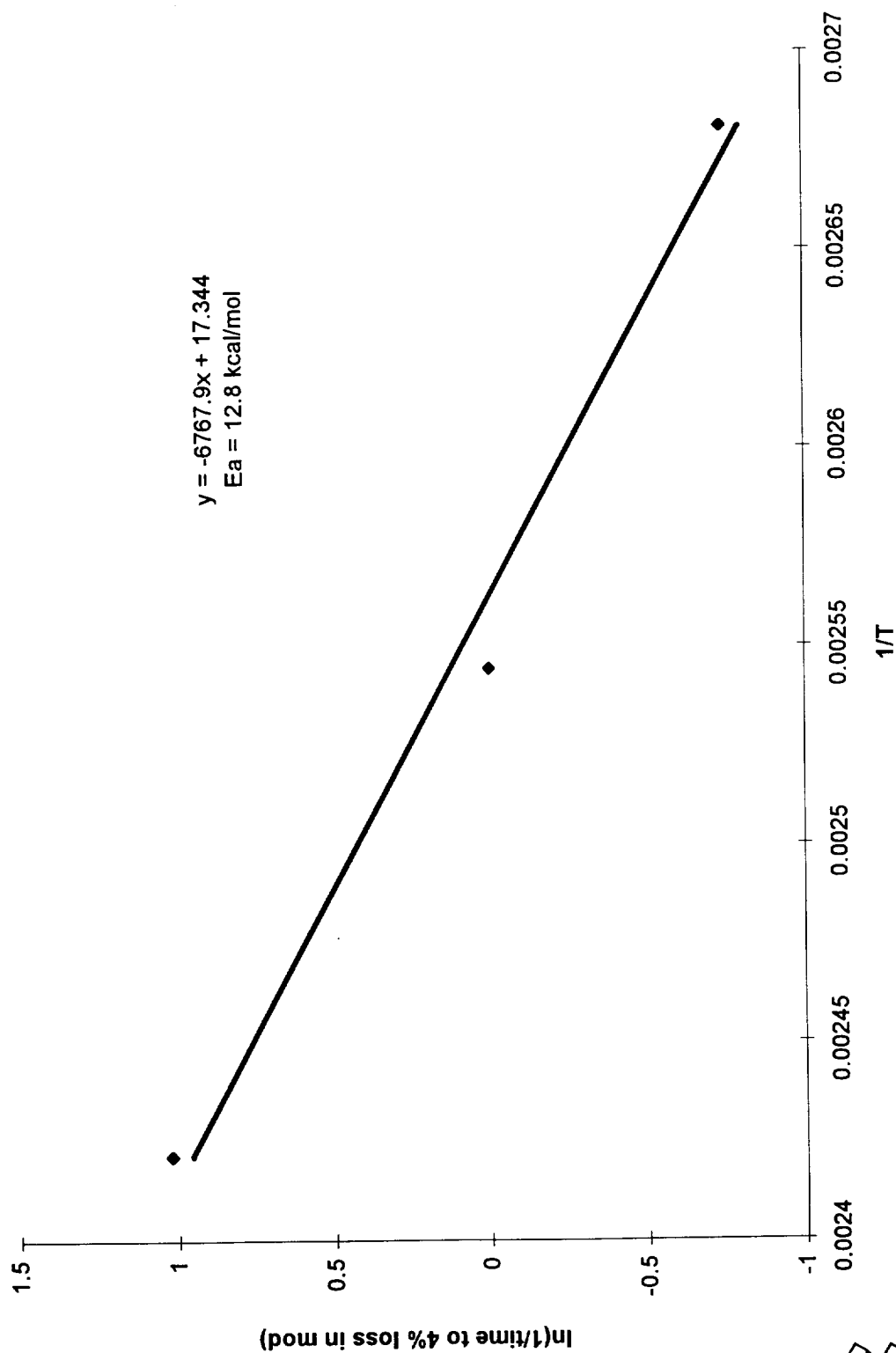


FIGURE 4a Arrhenius plot of modulus change (-4%) for Coflon after Fluid F exposure

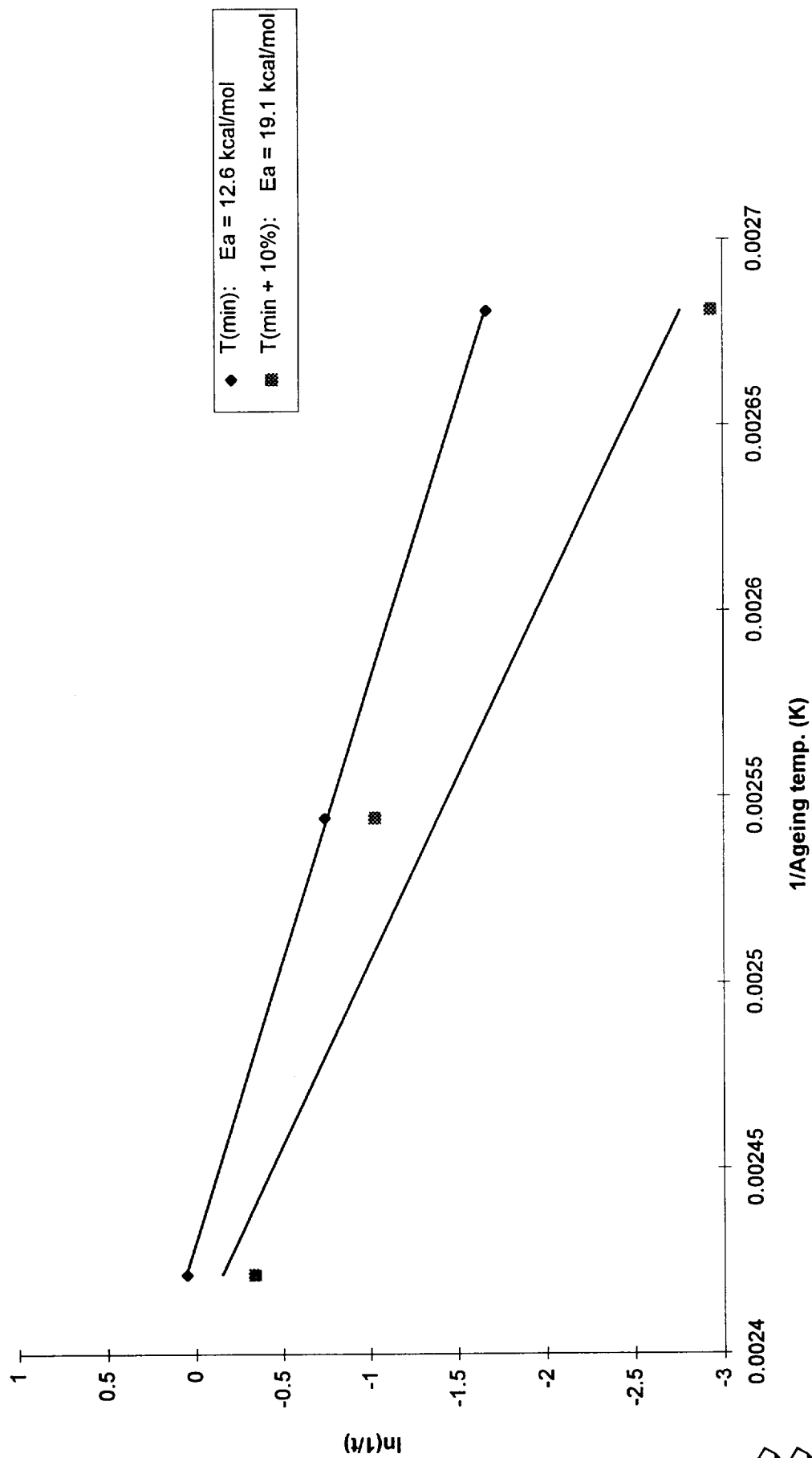


FIGURE 4b Arrhenius plot of Young's Modulus change for Coflon aged in Fluid F

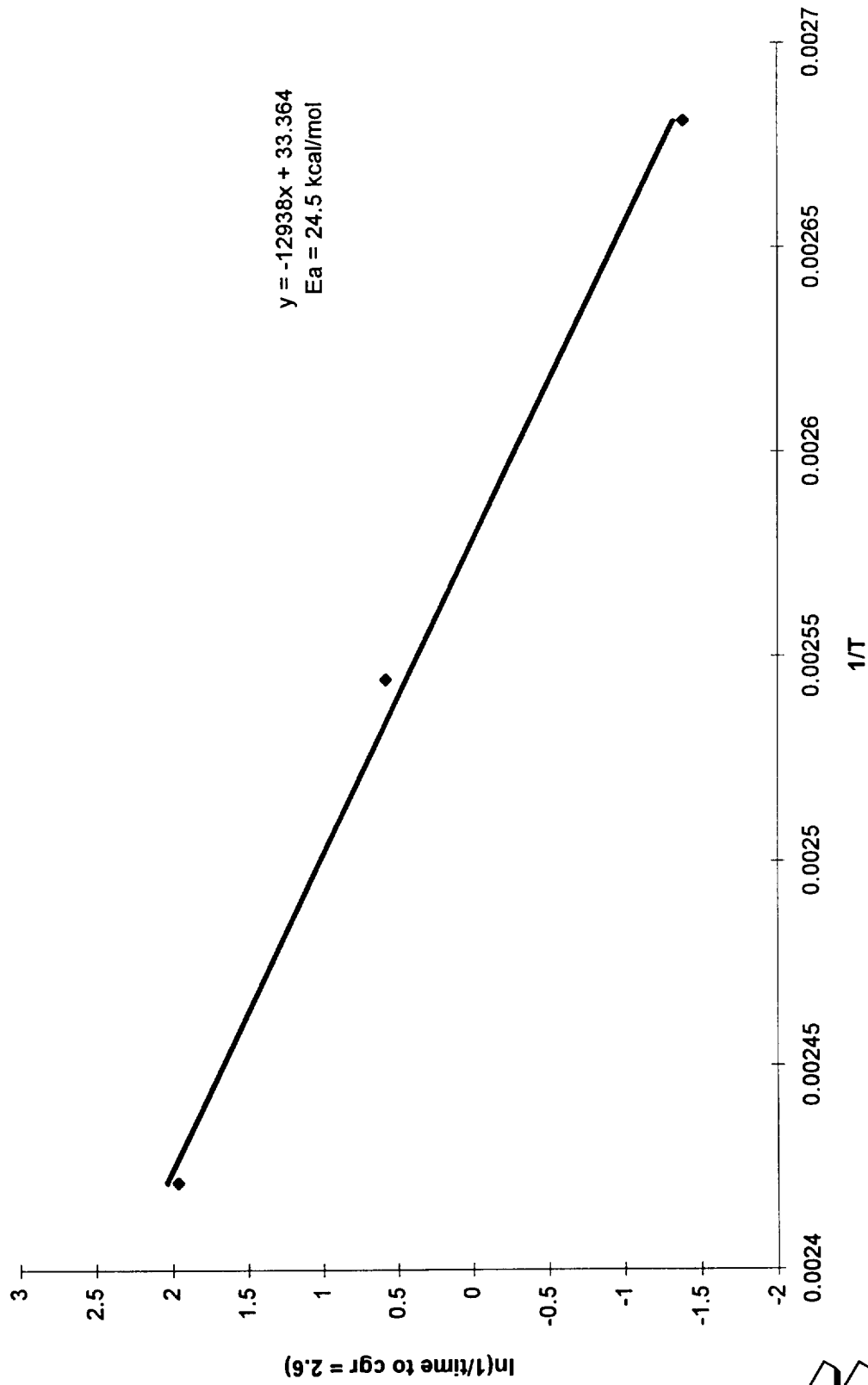


FIGURE 5a Arrhenius plot of change in crack growth resistance of Coflon after ageing in Fluid F

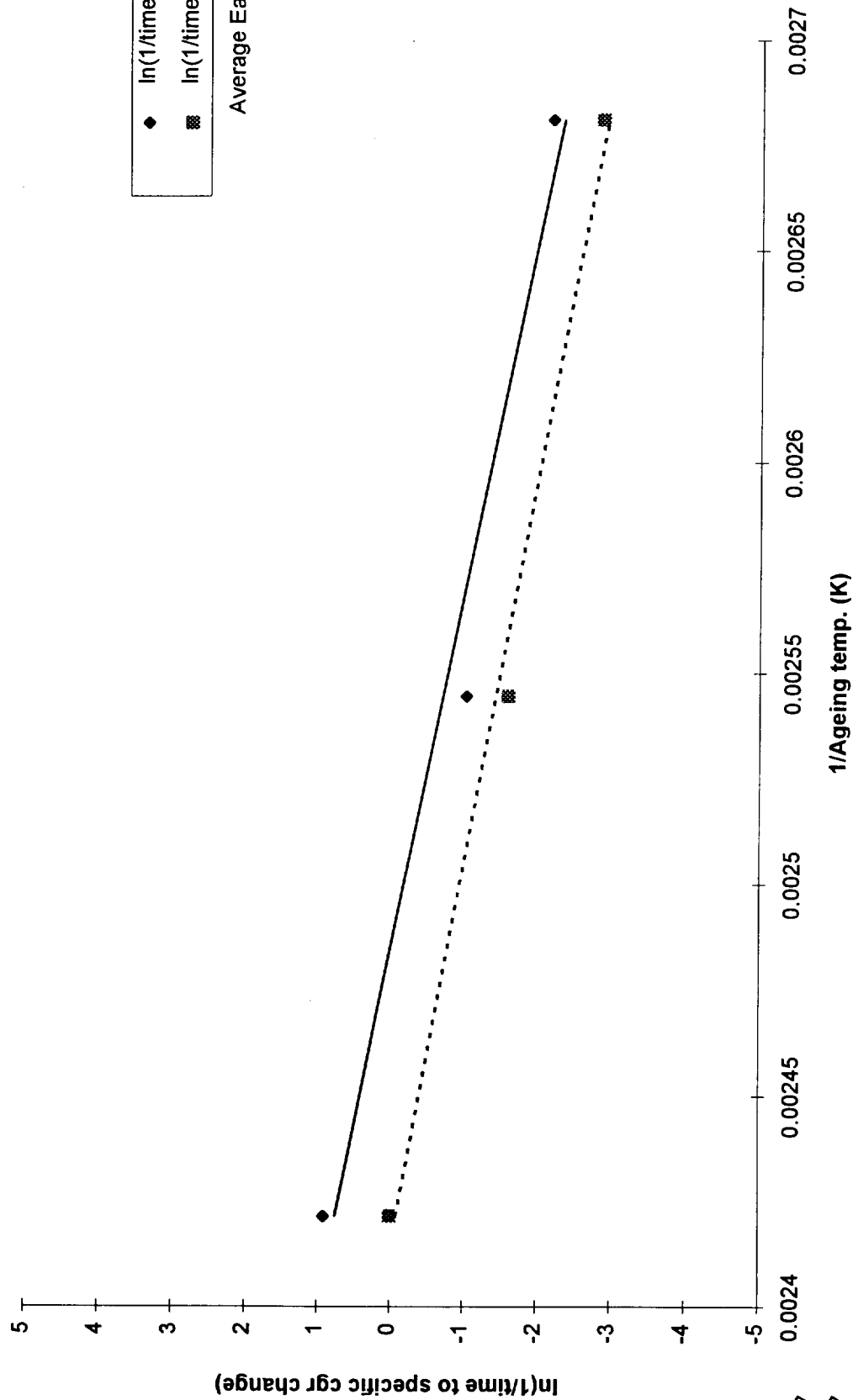


FIGURE 5b Arrhenius plots of crack growth resistance for Coflon aged in Fluid F

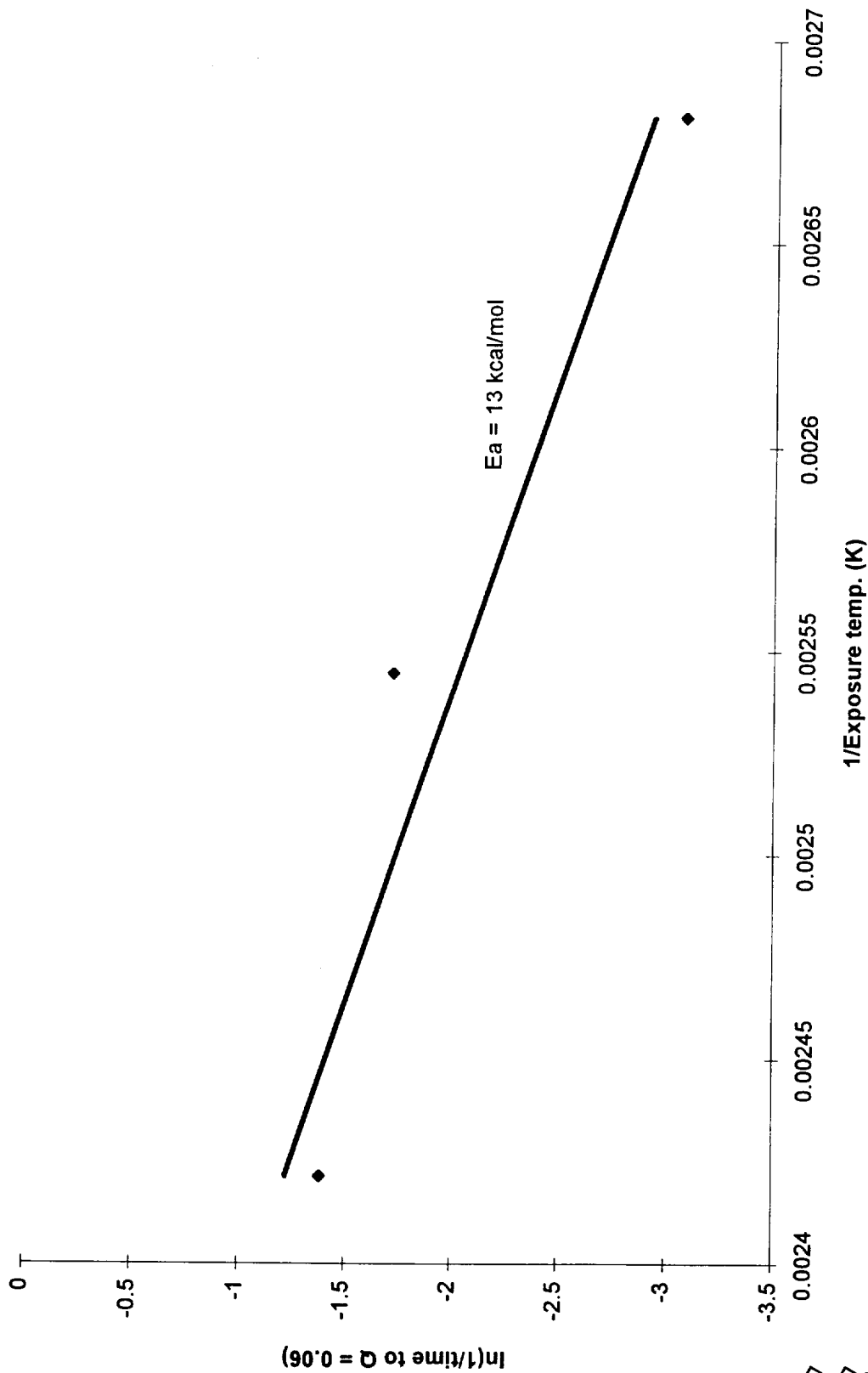


FIGURE 6 Arrhenius plot of change in permeation of methane through Coflon after ageing in Fluid F

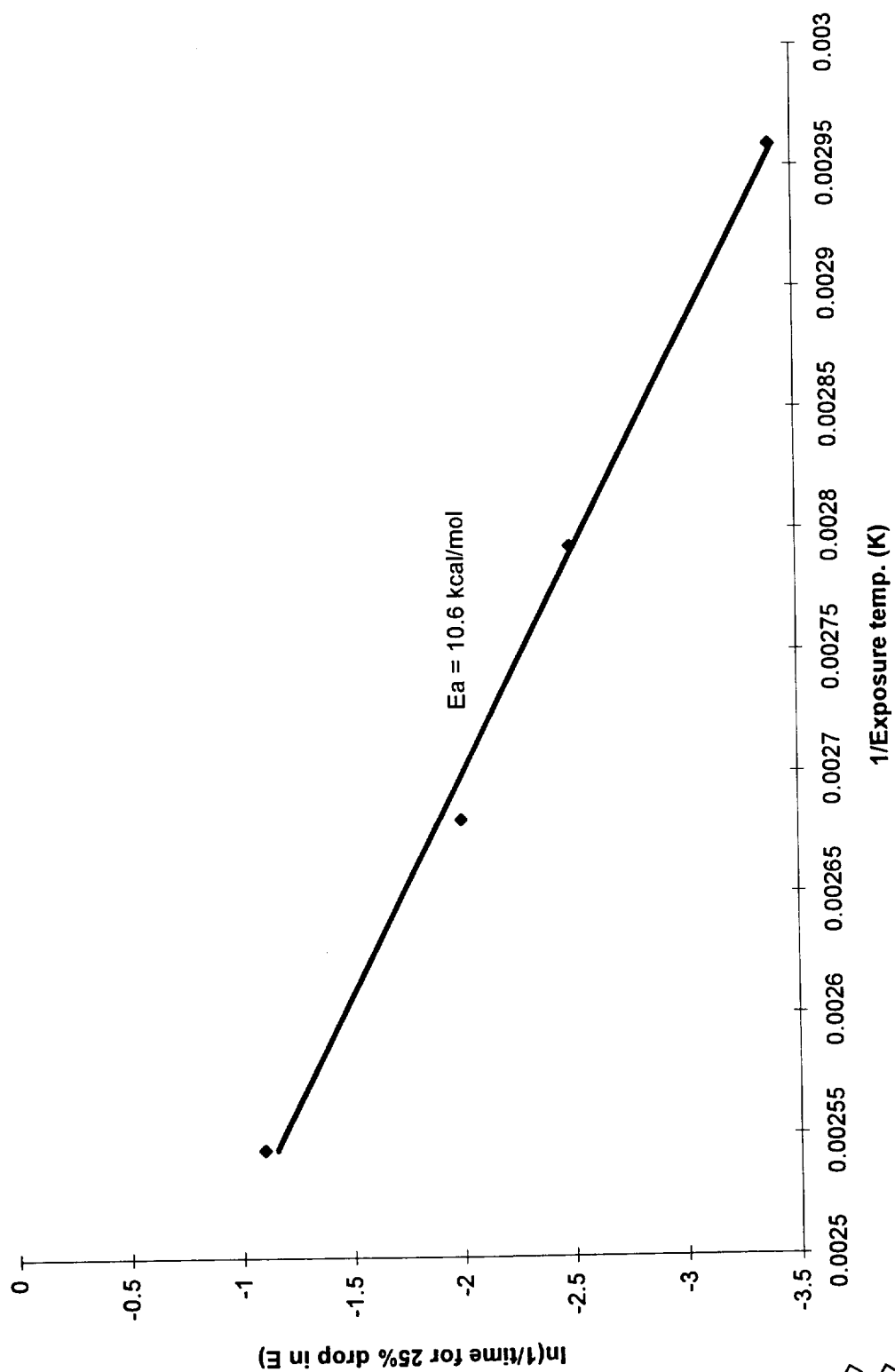


FIGURE 7 Arrhenius plot for Coflon aged in Fluid G - Moduli